(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 211 234 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.06.2002 Bulletin 2002/23

(51) Int Cl.7: **C07C 29/149**, C07C 31/20

(21) Application number: **01307942.1**

(22) Date of filing: **18.09.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **29.11.2000 KR 2000071643**
13.06.2001 KR 2001033142

(71) Applicants:
- **SAMSUNG ELECTRONICS CO., LTD.**
  Suwon-City, Kyungki-do 442-742 (KR)
- **Korea Research Institute of Chemical Technology**
  Daejun-si 305-390 (KR)

(72) Inventors:
- **Lee, Byeong No, Jungwoo Building 5th Floor**
  Seoul 131-222 (KR)
- **Lee, Jung Ho, 117/402 Hanbit Apartment**
  Daejun-Shi, 305-333 (KR)
- **Jang, Eun Joo, 111/908 Saejong Apartment**
  Yusung-Gu Daejun-Shi 305-390 (KR)
- **Kim, Hyung Rok, 6/207 Town Apartment**
  Jusung-Daejun-Shi, 305-340 (KR)
- **Han, Yo Han, 110/506 Hanbit Apartment**
  Daejun-Shi, 305-340 (KR)
- **Lee, Ho Sun**
  Chungnam-Do 330-160 (KR)
- **Shin, Hyun Kwan, 105/1704 Hanul Apartment**
  Daejun-Shi, 305-345 (KR)

(74) Representative: **Kyle, Diana**
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) Process for preparing 1,3-alkandiols from 3-hydroxyesters

(57) The present invention relates to a process for preparing 1,3-alkandiols from 3-hydroxyesters. More specifically, the present invention relates to a process for preparing 1,3-alkandiols from 3-hydroxyesters, which comprising hydrogenating 3-hydroxyesters in an alcohol-containing solvent in the presence of a novel hydrogenation catalyst, wherein said alcohol-containing solvent is a pure alcohol or a mixed solvent consisting of an alcohol and a high-boiling point solvent which boils at a higher temperature than the 1, 3-alkandiol does, and said catalyst was prepared by adding alkaline precipitator, such as alkali metal carbonates or sodium hydroxide, to an aqueous solution containing copper salt to form particles, and then ageing said particles following addition of colloidal silica thereto. According to the process of the present invention, 1,3-alkandiols can be selectively produced from 3-hydroxyesters in a high yield.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a process for preparing 1,3-alkandiols from 3-hydroxyesters. More specifically, the present invention relates to the preparation of 1,3-alkandiols from 3-hydroxyesters in a high yield as well as a process for preparing 1,3-alkandiols by hydrogenating 3-hydroxyesters in the presence of a hydrogenation catalyst.

[0002] 1,3-alkandiols have been widely used as coating materials or intermediates for various organic syntheses as well as raw materials for production of polyesters. At present, there are known several processes for preparing 1,3-alkandiols. For example, a process for preparing 1,3-alkandiols by hydroformylating epoxides into 3-hydroxyaldehyde derivatives and then hydrogenating the 3-hydroxyaldehyde derivatives has been used (See: US Patent Nos. 5,770,776, 5,723,389, 5,731,478 and 5,777,182). Further, a process for preparing 1,3-alkandiols by hydrating acrolein into 3-hydroxypropanal and then hydrogenating the resulting 3-hydroxypropanal has been also used (See: European Patent No. 577,972, US Patent No. 5,093,537). In addition to the above processes, another method has been reported to provide 1,3-alknaediols through a certain biological reaction, wherein glycerol is used as a starting material (See: European Patent No. 361,082, German Patent No. 3,734,764).

[0003] On the other hand, Shell Co. has commercially produced 1,3-propandiol through hydrogenation of 3-hydroxypropanal, which is prepared by hydroformylation of ethylene oxides. However, this process has disadvantages in that the unstable 3-hydroxypropanal is likely to oligomerize itself and many other side products including acetal are produced, so that hydrogenation into 1,3-propandiol cannot be properly completed and quality of the final product is lowered.

[0004] Even though an alternative process was suggested, wherein 1,3-alkandiols are prepared by carboesterifying epoxides with carbon monoxides and alcohols to produce 3-hydroxyesters and then hydrogenating the ester groups of the 3-hydroxyesters, it has not been put to practical use in the industrial field. This is due to that the reaction pathway thereof is very unselective for producing 1,3-alkandiols from 3-hydroxyesters when a conventional hydrogenation catalyst, such as copper-chromium oxide, copper-zinc oxide and Raney nickel, is used.

[0005] Meanwhile, many heterogeneous hydrogenation catalysts for gas-phase or liquid-phase processes have been proposed and actively used in the industrial field, which convert esters, carbonyl compounds, or C_4 or more dicarboxylic esters such as alkylmalate and cyclohexane dicarboxylic ester into their corresponding monoalcohols, 1,4-butandiol, and 1,4-cyclohexanedimethanol, etc. Such ester-hydrogenating catalysts can be found in, for example, US Patent No. 5,406,004. There are disclosed various Cu-containing catalysts, for example, including Cu-Al_2O_3 catalyst, reduced CuO/ZnO(Cu:Zn=0.4:1～2:1)-based catalyst, and reduced Cu-chromite(Cu:Cr=0.1:1～4:1)-based catalyst. In addition, there are also disclosed several catalysts modified with Ba, Mn, rare-earth metals(for example, La, Sm, Th, Ce, Y, etc.), Mg or Ca for 0.1～15 wt% of the CuO/ZnO or Cu-chromite catalysts. Moreover, some catalysts further comprising, if necessary, carriers such as alumina or zirconia are also well known in the art. All of the above catalysts are commercially available. Further, there are also known Pd-Zn catalyst (See: US Patent No. 5,185,476), Cu-TiO_2 catalyst (See: US Patent No. 4,929,777), Re-Cu-Zn catalyst (See: European Patent No. 373,946), Zn-Ru catalyst (See: US Patent No. 4,443,649), and Pd, Pt or Ru-containing catalyst.

[0006] Even though a number of Cu-containing catalysts and noble metal-containing catalysts have been studied and developed for use in preparing alcohols from their corresponding carbonyl group-containing compounds, particularly from esters, there have been proposed few catalytic processes useful for preparation of 1,3-alkandiols from 3-hydroxyesters having a hydroxyl group in the specific β-position. WO 00/18712 discloses use of a Cu/ZnO-based catalyst in preparation of 1,3-propandiol from methyl 3-hydroxypropionate, but it was found to have no meaningful catalytic activity in consideration of industrial applicability.

[0007] US Patent No. 4,973,769 and WO 99/38613 describe Cu-Al_2O_3-based catalyst and Ru-Re-based catalyst, respectively, as a catalyst to be used for preparing 1,2,4-butanetriol from malic acid or malic ester having a hydroxyl group in the β-position. In these references, however, relatively high pressure ranging from 100 to 300 atm is required as an essential reaction condition, so that these prior catalysts are unsuitable to be applied to a process for preparing the desired compounds of the present invention.

[0008] On the other hand, WO 00/18712 describes a method for hydrogenating methyl 3-hydroxypropionate to 1,3-propandiol in the presence of an alcohol solvent such as methanol. Although the alcohol solvent is expected to be able to suppress generation of lactones from 3-hydroxyesters and degradation of their ester groups, it is not helpful to maintain high selectivity at a high conversion rate and to ensure long-term reaction stability of the catalyst, since an alcohol having a low-boiling point exists as gas-phase under the flow of H_2 gas in a fixed bed reactor. In fact, significant decrease of the selectivity at a high conversion rate can be easily found in the Examples of the cited reference. Moreover, the boiling points and the other chemical properties, between the reactant, i.e., hydroxyesters and the product, i.e., 1,3-alkandiols, are so similar that isolation and purification of the product from the reactant are often difficult, which leads to problems in a practical process.

[0009] As compared with the hydrogenation of conventional esters, the hydrogenating process for 3-hydroxyesters substituted with a hydroxyl group at their β-position has problems in that: the reactants are chemically and thermally so unstable that dehydration of the hydroxyl groups at their β-position can readily occur, and the resulting unsaturated esters are easily reduced to generate undesirable side products such as saturated esters or corresponding monoalcohols wherein ester groups have been reduced. Additionally, β-lactone compounds generated from an intramolecular reaction of 3-hydroxyesters are thermally so unstable as to be degraded spontaneously or form lactone polymers, and they are converted into additional side products including various esters and lactone compounds through intermolecular reactions with the other reactants or through condensation reaction with 1,3-alkandiols which are derived from hydrogenation of 1,3- hydroxyesters. The extent to which these side reactions occur is affected by reaction temperature, so there is a limit in controlling the reaction rate by increasing the reaction temperature. However, keeping a high pressure in order to provide a moderate activity under a low temperature will also causes trouble in the industrial application.

[0010] A feature of the present invention is to provide a novel process for preparing 1,3-alkandiols from 3-hydroxyesters, wherein a novel hydrogenation catalyst exhibiting high catalytic activity as well as high selectivity even under a mild reaction condition is employed.

[0011] According to the present invention, there is provided a novel process for preparing 1,3-alkandiols from 3-hydroxyesters in a high yield, which comprising hydrogenating 3-hydroxyesters in an alcohol-containing solvent in the presence of a novel hydrogenation catalyst, wherein said alcohol-containing solvent is a pure alcohol or a mixed solvent consisting of an alcohol and a high-boiling point solvent which boils at a higher temperature than the 1, 3-alkandiol does, and said catalyst was prepared by adding alkaline precipitator, such as alkali metal carbonates or sodium hydroxide, to an aqueous solution containing copper salt to form particles, and then ageing said particles following the addition of colloidal silica thereto.

[0012] All of the above features and other features of the present invention will be successfully achieved from the present invention described in the following.

[0013] According to the present invention, Cu-containing catalyst stabilized with silica is applied to a hydrogenation process for preparing 1,3-alkandiols from 3-hydroxyesters. The major component of the catalyst is Cu in the form of oxide, whose content in the catalyst is 20～99% by weight, preferably 50～95% by weight, and content of silica in the catalyst is 1～80% by weight, preferably 5～50% by weight. The silica-stabilized copper oxide catalyst as described above can be represented by $CuO\text{-}SiO_2$. The catalyst of the present invention cannot be obtained by any of the typical impregnation processes using a conventional silica carrier, and thus it should be made by a particular method which comprising stabilizing micro-particles (diameter □ 10nm) of copper oxide precursor with silica in order to achieve the desired high catalytic activity. More specifically, the catalyst used in the present invention is prepared by a novel method which comprising adding alkaline precipitator, such as alkali metal carbonates or sodium hydroxide, to an aqueous solution containing copper salt, and then ageing the resulting copper hydroxide particles with colloidal silica. Significantly, the silica contained in the catalyst of the present invention would act as an essential component, and therefore it is clearly discriminated from the conventional carriers.

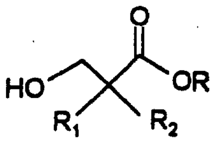
[0014] In the present invention, any of the conventional extruding or pelleting method and impregnating method using thermal-resistant carriers may be applied to forming said catalyst. The formed catalyst is then calcined for 2～10 hrs at a temperature ranging from 200 to 800°C, preferably 300 to 700°C.

[0015] The oxide catalyst thus obtained may be used preferably after activation with hydrogen or hydrogen-containing gas at a temperature ranging from 150 to 450°C for 1～20 hours. In general, this activation step is performed while flowing the hydrogen or hydrogen-containing gas diluted with nitrogen or argon gas into a reactor filled with the calcined oxide catalyst. At this time, concentration of hydrogen, flow rate of the input gas, and temperature-increasing rate, etc. should be carefully controlled in order to prevent the catalyst from being sintered by heat generated in the course of its reduction.

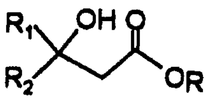
[0016] The hydrogenation catalyst may be used in combination with one or more promoters in order to improve its hydrogenation activity and selectivity. As useful promoters, Re, Ru, Pd, Pt, Rh, Ag, Se, Te, Mo and Mn are preferred, and their content in the catalyst should be 0.001～10 mol%, preferably 0.003～7 mol% based on Cu.

[0017] Alternatively, the hydrogenation catalyst of the present invention may be used after modification using alkylsilane compounds in order to improve its catalytic activity and selectivity. At this time, hydroxyl groups of silica are masked with the alkylsilane compounds. In the present invention, trialkoxymonoalkylsilane, dialkoxydialkylsilane or monoalkoxytrialkylsilane, wherein the alkyl group(s) consists of 1 to 30 carbon atoms, and the alkoxy group(s) is linear or non-linear alkoxy group, preferably methoxy or ethoxy group, is used as the alkylsilane compound. Preferred alkylsilane compounds include, without limitation, trimethoxypropylsilane, trimethoxyoctylsilane, dimethoxydimethylsilane, dimethoxymethylpropylsilane, dimethoxymethyloctylsilane, methoxytrimethylsilane, methoxydimethylpropylsilane and methoxydimethyloctylsilane.

[0018] 3-hydroxyesters used in the hydrogenation reaction according to the present invention can be represented by the following formula (I) or (II):



(I)



(II)

[0019] In the above formulas (I) and (II), R_1, R_2 and R are independently hydrogen atom, $C_{1\sim20}$ non-branched saturated aliphatic hydrocarbon, branched aliphatic hydrocarbon, saturated cyclic hydrocarbon, hydrocarbon chain containing a ring structure, or hydrocarbon substituted with ester, hydroxyl or alkoxy group for hydrogen atom at one or more carbon chains of the above hydrocarbon species.

[0020] In the above formulas (I) and (II), R of the ester group is preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutenyl, t-butyl, cyclohexyl, or cyclohexane methyl.

[0021] Preferred examples of said 3-hydroxyesters include methyl(or ethyl) 3-hydroxypropionate, 3-hydroxybutyric ester, 3-hydroxypentanoic ester, 3-hydroxyheptanoic ester, 3-hydroxyoctanoic ester, 3-hydroxynonanoic ester, 3-hydroxydecanoic ester, 2-methyl-3-hydroxypropanoic ester, 2-methyl-3-hydroxybutanoic ester, 2-methyl-3-hydroxypentanoic ester, 2-methyl-3-hydroxyhexanoic ester, 2-methyl-3-hydroxyheptanoic ester, 2-methyl-3-hydroxyoctanoic ester, 2-methyl-3-hydroxynonanoic ester, 2-methyl-3-hydroxydecanoic ester, 2-ethyl-3-hydroxybutanoic ester, 2-ethyl-3-hydroxypentanoic ester, 2-ethyl-3-hydroxyhexanoic ester, 2-ethyl-3-hydroxyheptanoic ester, 2-ethyl-3-hydroxyoctanoic ester, 2-ethyl-3-hydroxynonanoic ester, 2-ethyl-3-hydroxydecanoic ester, etc..

[0022] According to the present invention, any type of the conventional hydrogenation processes such as liquid-phase slurry process, liquid-gas phase process and gas-phase process can be applied to preparing 1,3-alkandiols from said 3-hydroxyesters by using the hydrogenation catalyst of the present invention.

[0023] According to the process of the present invention, it is possible to directly supply 3-hydroxyesters together with H_2 gas to the hydrogenation catalyst. However, it is much preferred to supply 3-hydroxyesters dissolved in an alcohol solvent or a mixed solvent consisting of an alcohol and a high-boiling point solvent whose boiling point is higher than those of the reactant and the product in light of that: (i) side reactions including intramolecular reaction of the reactant, i.e., 3-hydroxyesters, and generation of lactones or condensation reaction between the reactant and the product can be suppressed, (ii) catalytic activity and selectivity of the catalyst can be enhanced by controlling concentration of the reactant to contact the catalyst during the reaction, and (iii) significant decrease of selectivity at a high conversion rate can be relieved.

[0024] Particularly for the liquid-gas phase process, 3-hydroxyesters are supplied as being dissolved in a mixed solvent consisting of an alcohol and a high-boiling point solvent as described above. At this time, the alcohol and the high-boiling point solvent are mixed together in the ratio of 5:95$\sim$90:10(w/w), preferably 10:90$\sim$70:30(w/w), and final concentration of 3-hydroxyesters in the whole reaction mixture should be 2$\sim$95%, preferably 5$\sim$90% by weight.

[0025] According to the liquid-gas phase process, the hydrogenation catalyst is filled in a reactor, and then both H_2 gas having a relatively low partial pressure and said 3-hydroxyester-containing solution are flowed simultaneously in the same direction into the reactor, so that H_2 gas may react with liquid-phase 3-hydroxyesters. This process is preferred in that retention time can be easily controlled.

[0026] As for the desirable reaction conditions for such liquid-gas phase process, reaction temperature ranges from 100 to 250°C, preferably 120 to 200°C, and reaction pressure ranges from 50 to 3,000 psig, preferably 150 to 2,000 psig. Further, flow rate of the 3-hydroxyester-containing solution into the reactor is controlled so that LHSV can be in the range of 0.01$\sim$5 hrs^{-1}, preferably 0.03$\sim$3 hrs^{-1} when calculated for only the 3-hydroxyesters. The amount of H_2 gas is also controlled so that molar ratio of H_2 to 3-hydroxyesters can be in the range of 10$\sim$300:1, preferably 20$\sim$200:1.

[0027] Alternatively, when 3-hydroxyesters are hydrogenated by the gas-phase process, they are supplied as being dissolved in an alcohol solvent. At this time, mixing ratio of 3-hydroxyesters and the alcohol solvent should be in the range of 10:90$\sim$90:10(w/w), preferably 30:70$\sim$70:30(w/w).

[0028] According to the gas phase process, the hydrogenation catalyst is filled in a reactor, and then both H_2 gas having a relatively high partial pressure and said 3-hydroxyester-containing solution are flowed simultaneously in the same direction into the reactor, so that 3-hydroxyesters, in a evaporated state, may react with H_2 gas.

[0029] As for the desirable reaction conditions for such gas phase process, reaction temperature ranges from 130 to 200°C, preferably 140 to 200°C, and reaction pressure ranges from 100 to 3,000 psig, preferably 200 to 1,500 psig. Further, flow rate of the 3-hydroxyester-containing solution into the reactor is controlled so that LHSV can be in the range of 0.02~1.0 hrs^{-1}, preferably 0.05~0.20 hrs^{-1} when calculated for only the 3-hydroxyesters. The amount of H_2 gas is also controlled so that molar ratio of H_2 to 3-hydroxyesters can be in the range of 300~3,000:1, preferably 500~1,500:1. The gas phase process performed under these conditions would result in a very high conversion rate up to 99% or more without decrease of selectivity.

[0030] The alcohol which can be used in the above processes is not limited to a specific one, but $C_{1\sim5}$ linear or non-linear alcohols, such as methanol, ethanol, propanol, isopropanol, n-butanol, isobutanol, t-butanol, etc., are preferred. A low-boiling point alcohol such as methanol, which boils a lower temperature than 1,3-alkandiol does, is preferred particularly for the gas-phase process.

[0031] As the high-boiling point solvent, any solvent can be used, provided that it can be readily mixed with 3-hydroxyester compound and has a boiling point higher than that of 1,3-alkandiol so that it can be readily separated therefrom. However, it is preferable to use an ether compound such as tetra(ethylene glycol)dimethyl ether (hereinafter, referred to as "TEGDME"), penta(ethylene glycol)dimethyl ether and sulfolane.

[0032] While preparing 1,3-alkandiols from 3-hydroxyesters in the presence of the hydrogenation catalyst of the present invention, the reaction condition should be appropriately controlled so that conversion rate per pass can be maintained in the range of 30~99%, preferably 60~98%, and more preferably 80~98%. If the reaction is carried out under a stringent condition for maintaining the conversion rate over 99%, selectivity of the reaction will decrease, which is undesirable. In order to increase the conversion rate, various methods, for example, including a method wherein a part of the reaction product is isolated and successively recirculated without any additional separate purification step, and a method wherein the reaction product is isolated and purified, and then both unreacted 3-hydroxyesters and side products derived from transesterification are recirculated to the hydrogen reaction, may be adopted.

[0033] The present invention can be more clearly understood with referring to the following examples. It should be understood that the following examples are not intended to restrict the scope of the present invention in any manner.

Example 1

(1) Preparation of a hydrogenation catalyst CuO(70 wt%)-SiO_2(30 wt%)

[0034] To a solution containing 60.0g of [$Cu(NO_3)_2 \cdot 3H_2O$] in 400ml of distilled water was added 124ml of aqueous NaOH solution(16 wt%) to form precipitates. 21.2g of colloidal aqueous silica solution, Ludox AS-40(ammonium-stabilized type, 40 wt% of silica) was added thereto, and then the precipitates were allowed to age at 70~80°C for 4 hrs. The precipitates were recovered by filtration, washed with deionized water, and then dried at 120°C for 12 hrs. Then, the catalyst powder thus obtained was shaped by pressing and crushed again into particles of 20~40 mesh size. The catalyst particles were calcined at 450°C under atmosphere for 6 hrs. The calcined copper oxide catalyst was analyzed by XRD(XRD line broadening method), and crystal size and BET surface area of copper oxide were found to be 4.5nm and $172m^2/g$, respectively.

(2) Activation of the catalyst

[0035] In a tube-shaped reactor(1.27cm in external diameter, 25cm in length), the copper oxide catalyst(3.0g) obtained from the above was filled, and then temperature of the reactor was elevated to 300°C at a rate of 0.5°C /min with flowing 5% H_2/N_2 mixed gas thereto. Then, the catalyst was reduced at 300°C for 6 hrs.

(3) Hydrogenation reaction of methyl 3-hydroxypropionate

[0036] After activating the catalyst by reduction as described above, temperature of the reactor was cooled to 150°C, and pressure in the reactor was adjusted to 900 psig. Then, H_2 gas was flowed into the reactor at a rate of 90ml/min, and a reactant mixture consisting of methyl 3-hydroxypropionate(MHP):methanol:TEGDME=20:20:60(w/w/w) was introduced thereto via a HPLC pump at a flow rate of 0.015ml/min in the same direction as that of H_2 gas. The resulting product was sampled under the pressured condition at intervals and subjected to GC analysis. At the point after 50 hrs from initiation of the reaction, conversion rate of MHP was 90.26% and selectivity for 1,3-propandiol was 88.51%.

Comparative Example 1

[0037] The procedure of Comparative Example 1 was conducted according to the same manner as in the above Example 1(3), except that a reactant mixture consisting of methyl 3-hydroxypropionate(MHP):methanol=20:80(w/w) was used instead of that consisting of methyl 3-hydroxypropionate (MHP):methanol:TEGDME=20:20:60(w/w/w). In case of this reaction, conversion rate of MHP was 81.21% and selectivity for 1,3-propandiol was 74.60%.

Example 2

[0038] Hydrogenation catalyst, CuO(80 wt%)-SiO_2(20 wt%) was prepared according to the same manner as in the above Example 1(1). To 10g of the catalyst powder calcined at 450°C was added a solution containing 0.163g of Re_2O_7 in acetone, and then the catalyst powder was subjected to ball-milling. Then, acetone was vaporized at room temperature, and the remaining powder was further dried at 120°C. The dried catalyst powder was shaped by pressing and crushed again into particles of 20~40 mesh size. In a reactor, 3.0g of the resulting catalyst particles was filled and reduced at 200°C according to the same manner as in the above Example 1(2), except that pure H_2 gas, not H_2/N_2 mixed gas, was introduced into the reactor. With employing thus activated catalyst further comprising Re as a promoter, hydrogenation reaction was performed under the condition as described in the following Table 1. The results are summarized in Table 1.

Examples 3-8

[0039] Hydrogenation catalyst, CuO(80 wt%)-SiO_2(20 wt%) was prepared according to the same manner as in the above Example 1(1), which was primarily calcined at 300°C. Then hydrogenation catalysts further comprising Pd, Ru, Ag, Se, Te or Mo as a promoter were prepared according to the same manner as in the above Example 2, except varying the precursor compound for corresponding promoter as follows: $Pd(NO_3)_2 \cdot 2.5H_2O$ dissolved in distilled water was used as Pd precursor; $Ru_3(CO)_{12}$ dissolved in ethanol was used as Ru precursor; and each of $AgNO_3$, $(NH_4)_2SeO_4$, $(NH_4)_2TeO_4$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ dissolved in distilled water was used as Ag, Se, Te and Mo precursors, respectively. Each of the resulting catalysts was dried at 120°C, and then calcined at 450°C for 6 hrs. The calcined catalysts were activated by reduction as described in Example 1(2). Hydrogenation reactions were conducted under the conditions as described in the following Table 1. The results are summarized in Table 1.

Example 9

[0040] Hydrogenation catalyst, $Mn_{0.61}Cu_{10}SiO_2$ was prepared according to the same manner as in the above Example 1(1), except adding aqueous NaOH solution to an aqueous solution containing both $Cu(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ to form co-precipitates. The resulting catalyst was activated as described in Example 1(2), and then hydrogenation reaction was conducted under the conditions as described in the following Table 1. The results are summarized in Table 1.

Table 1

	Catalyst[1]	Reaction condition				Conversion Rate of MHP(%)	Selectivity for 1,3-propandiol (%)
		Temp. (°C)	Pressure (psig)	Rate of supplying H_2 gas (ml/min)	Rate of supplying reactants[2] (ml/min)		
Example 2	$Re_{0.067}Cu_{10}SiO_2$	150	900	90	0.015	94.1	88.12
Example 3	$Pd_{0.040}Cu_{10}SiO_2$	150	1,000	90	0.015	94.86	89.63
		155	1,000	90	0.020	91.97	88.36
Example 4	$Ru_{0.038}Cu_{10}SiO_2$	150	1,000	90	0.015	97.06	85.72
		155	1,000	90	0.020	92.98	87.37
		155	1,000	90	0.025	85.42	88.08

1) The subscripts represent atomic ratios between the promoters and Cu.

2) MHP:MeOH:TEGDME=20:20:60(w/w/w)

Table 1 (continued)

	Catalyst[1)]	Reaction condition				Conversion Rate of MHP(%)	Selectivity for 1,3-propandiol (%)
		Temp. (°C)	Pressure (psig)	Rate of supplying H_2 gas (ml/min)	Rate of supplying reactants[2)] (ml/min)		
Example 5	$Ag_{0.022}Cu_{10}SiO_2$	155	900	90	0.015	96.70	84.28
Example 6	$Se_{0.018}Cu_{10}SiO_2$	150	1,000	90	0.015	92.03	87.04
Example 7	$Te_{0.013}Cu_{10}SiO_2$	150	1,000	90	0.015	94.81	87.33
Example 8	$Mo_{0.07}Cu_{10}SiO_2$	150	1,000	90	0.0175	92.55	88.01
		155	1,000	90	0.0175	97.92	88.43
Example 9	$Mn_{0.61}Cu_{10}SiO_2$	150	1,000	90	0.0175	96.69	88.78
		145	1,000	90	0.0175	82.90	87.70

1) The subscripts represent atomic ratios between the promoters and Cu.
2) MHP:MeOH:TEGDME=20:20:60(w/w/w)

Example 10

[0041] Hydrogenation catalyst, CuO(80 wt%)-SiO_2(20 wt%) was prepared according to the same manner as in the above Example 1(1). 10.0g of the catalyst powder calcined at 450°C for 6 hrs was suspended in toluene under argon atmosphere, and then 1.5g of trimethoxyoctylsilane was added thereto. Then reaction was conducted for 2 hrs with refluxing toluene, and the resulting catalyst powder was rinsed with toluene and dried. The dried catalyst powder was shaped by pressing and crushed again into particles of 20~40 mesh size. In a reactor, 3.0g of the catalyst particles was filled and primarily reduced with 5% H_2/N_2 mixed gas while slowly elevating temperature of the reactor to 200°C. Then, H_2 gas was introduced into the reactor to 900 psig, and temperature of the reactor was adjusted to 150°C, and then hydrogenation reaction was performed under the same condition as described in Example 1(3). The results are summarized in the following Table 2.

Table 2

Reaction condition				Conversion rate of MHP (%)	Selectivity for 1,3-propandiol (%)
Rate of supplying reactants[1)] (mi/min)	Rate of supplying H_2 gas (ml/min)	Temperature (°C)	Pressure (psig)		
0.015	90	150	950	97.41	87.50
0.017	90	150	1,000	98.29	87.15
0.0185	90	150	1,000	94.72	88.86
0.0225	90	155	1,000	98.24	86.26
0.025	90	155	1,000	95.39	86.23

1) MHP:MeOH:TEGDME=20:20:60(w/w/w)

Example 11

[0042] Hydrogenation catalyst, CuO(80 wt%)-SiO_2(20 wt%) was prepared according to the same manner as in the above Example 1(1). In a reactor, 3.0g of the catalyst was filled, and then activated by reduction as described in Example 1(2). Hydrogenation reaction was carried out by using the activated catalyst as follows: H_2 gas was flowed into the reactor at a rate of 90ml/min to 1000 psig at 155°C, and a reactant mixture consisting of methyl 3-hydroxybutyrate(MHB):methanol:TEGDME=20:20:60(w/w/w) was introduced thereto at a flow rate of 0.015ml/min in the same direction as that of H_2 gas. As a result, it could be found that conversion rate of MHB was 82.85% and selectivity for 1,3-butandiol was 74.35%.

Example 12

[0043] Hydrogenation catalyst, CuO-Mn-SiO_2 was prepared and reduced according to the same manner as in the above Example 9. Then hydrogenation reaction was conducted under the different conditions as described in the following Table 3, while flowing a reactant mixture consisting of methyl 3-hydroxypropionate(MHP):methanol= 40:60 (w/w) into a reactor filled with the catalyst. The results are summarized in Table 3.

Table 3

Reaction condition				Conversion rate of MHP (%)	Selectivity(%)			
Temperature (°C)	Pressure (psig)	LHSV (hr^{-1})	H_2/MHP (mol/ mol)		PDO	1-Propanol	Methyl propionate	The others
155	600	0.096	900	98.77	88.79	7.23	2.29	1.69
155	600	0.107	810	97.46	89.12	6.04	2.32	2.52
153	750	0.107	850	99.13	89.07	6.61	2.80	1.52
153	750	0.096	950	99.35	89.06	6.74	2.55	1.11
160	450	0.129	670	95.08	85.98	7.71	3.72	2.59
160	600	0.129	670	97.94	86.07	8.0	3.54	2.39

[0044] The present invention is to provide a novel process for preparing 1,3-alkandiols through hydrogenating 3-hydroxyesters. According to the process of the present invention, by employing unique hydrogenation catalyst in a certain reaction system, 1,3-alkandiols can be selectively produced in a high yield.

Claims

1. A process for preparing a 1,3-alkandiol, which comprises hydrogenating a 3-hydroxyester in the presence of a catalyst to form a 1,3-alkandiol wherein the catalyst was prepared by adding an alkaline precipitator to an aqueous solution containing copper salt to form particles and then ageing said particles following the addition of colloidal silica thereto.

2. The process according to claim 1, wherein the alkaline precipitator is an alkali metal carbonate or sodium hydroxide.

3. The process according to claim 1 or 2, wherein the catalyst comprises CuO and SiO_2 in the ratio of 9:1 to 5:5 by weight.

4. The process according to any of claims 1 to 3, wherein the catalyst further comprises one or more promoters selected from Re, Pd, Ru, Pt, Rh, Ag, Se, Te, Mo and Mn in a content of 0.001 to 10 mol% based on Cu.

5. The process according to any of claims 1 to 4, wherein the catalyst is modified with one alkylsilane compound selected from trialkoxymonoalkylsilane, dialkoxydialkylsilane and monoalkoxytrialkylsilane, wherein each alkyl group independently consists of 1 to 30 carbon atoms, and each alkoxy group is independently methoxy or ethoxy

group.

6. The process according to any of claims 1 to 5, wherein the 3-hydroxyester is methyl 3-hydroxypropionate.

7. The process according to any of claims1 to 6, wherein the hydrogenation reaction is carried out by a liquid-gas phase process in a mixed solvent consisting of an alcohol and a high-boiling point solvent which boils at a temperature higher than the boiling point of 1,3-alkandiol.

8. The process according to claim 7, wherein the high-boiling point solvent is tetra(ethylene glycol)dimethyl ether, penta(ethylene glycol)dimethyl ether or sulfolane, and the weight ratio of the alcohol to the high-boiling point solvent ranges from 5:95 to 90:10(w/w).

9. The process according to any of claims 1 to 8, wherein the 3-hydroxyester is dissolved in the mixed solvent to a concentration of 2 to 95% by weight.

10. The process according to any of claims 1 to 9, wherein the hydrogenation reaction is carried out at a temperature of 100 to 250°C under a pressure of 50 to 3,000 psig in a fixed bed reactor.

11. The process according to any of claims 1 to 10, wherein the hydrogenation reaction is performed while maintaining the molar ratio of the introduced H_2 gas to the 3-hydroxyester in the range from 10:1 to 300:1 (m/m).

12. The process according to any of claims 1 to 6, wherein the hydrogenation reaction is carried out by a gas phase process in a low-boiling point alcohol solvent which boils at a temperature lower than the boiling point of 1,3-alkandiol.

13. The process according to claim 12, wherein the low-boiling point alcohol solvent is methanol.

14. The process according to claim 12 or 13, wherein the weight ratio of the 3-hydroyester to the alcohol solvent ranges from 10:90 to 90:10(w/w).

15. The process according to any of claims 12 to 14, wherein the hydrogenation reaction is carried out at a temperature of 130 to 200°C under a pressure of 100 to 3,000 psig in a fixed bed reactor.

16. The process according to any of claims 12 to 15, wherein the hydrogenation reaction is carried out while maintaining the molar ratio of the introduced H_2 gas to the 3-hydroxyester in the range from 300:1 to 3,000:1(m/m).